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The inventor will be declared later

(56) References cited

DE	27 14 939 B2
WO	97 32 208 A1

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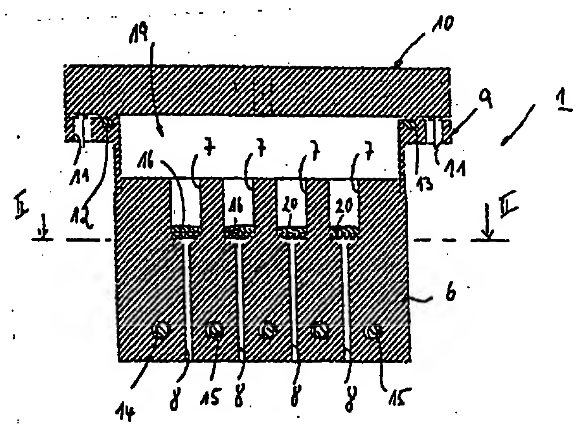
(54) A device for testing the catalytic activity of solids exposed to reaction gases

(57) An apparatus for testing the catalytic activity of a solid exposed to a reaction gas has a receiving device (1) which has a plurality of recesses (7) for receiving each individual solid, a common gas supply, and passages (8) connected to each recess so that all solids are simultaneously exposed to the reaction gas, and the products formed as a result of the reaction can be discharged separately through the passages and can be supplied to an analysis device. The recesses for receiving the solids are arranged as a matrix. The test apparatus also has a loading device which is used to transfer in a simple way catalysts which are prepared in a spatially separate manner by the combinatorial method into the recesses of the receiving device.



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Description

The invention relates to an apparatus for testing the catalytic activity of solids exposed to a reaction gas having a receiving device for receiving a solid and a device for analysis of products released as a result of the reaction.

For the production and assessment of catalysts, potentially active carrier and catalyst components are combined in presumably appropriate manner, and the resulting multiple-component mixture is tested with an appropriate test reaction under predetermined conditions which are mainly determined by technical limitations. During synthesis of such materials, it is often necessary to meet the time requirements, because the testing of catalysts is a time and labor consuming operation. Generally, a material that is being tested is loaded into a laboratory reactor designed for this purpose and is tested for its ability to catalyze the reaction of feed mixtures.

EP 0 423 294 B 1 discloses an apparatus for study and evaluation of fluidized bed cracking catalysts which are used exclusively in tubular reactors. The prior art apparatus is used for conducting a number of continuous cyclic experiments under varying experimental conditions.

It is also known to test catalysts in a plurality of separate reactors which have provisions for a general gas purification. When catalysts are tested in parallel reactors, the charging of the catalysts with the materials being tested is a time and labor consuming operation. Another disadvantage is that the quantity of the reactors that have to be used for the parallel operation is limited by practical considerations.

A decisive innovation of recent in the field of bioorganic synthesis has been the development of the combinatorial synthesis processes (Furka, A., Sebastien, E, Asgedom, M., Dibo, G., Abstr. - 14th Int. Congr. Biochem., Prague 1988, Vol. 5, 47). In conducting such synthesis processes, they mainly deal with very small quantities of substances, and polymer carriers are often used for fixation of reagents and the resulting products. Thus the combinatorial synthesis is now a standard tool in the bioorganic chemistry. The efficient testing of a set of substances which could be prepared by using such synthesis process is normally done nowadays by using so-called "high throughput screening", in testing potential pharmaceuticals. The state-of-the art testing methods are based on adding individual substances of a bank of substances to enzymes or a cell cultures, which show the possibility of interaction between the substance and a predetermined active position of the enzyme or cell material growth by means of a luminescence examination. The substances from a bank set of substances are placed in so called "arrays", under plates with recesses which are used as reaction vessels and are contacted with appropriate test systems, after which the sample is post-processed (irradiation, incubation, etc.), with subsequent assessment testing.

The fist disclosure of the conduct of the combinatorial synthesis and testing process was made in

1995 by Schultz et al. (Xiang, X. -D., Sun, X., Briceno, G., Lou, Y., Wang, K.-A., Chang, H., Wallace-Freedman, W.-G., Chen, S.-W, Schultz, P. G., Science 268, 1995, 1738 and Briceno, G,, Chang, H., Sun, X., Schultz, P. G., Xiang, X.-D., Science 270, 1995, 273, as well as Sun, X.-D., Wang, K.-A., Yoo, Y., Wallace-Freedman, W. G., Gao, C., Xiang, X. -D., Schultz, P. G., Adv. Mater. 9, No. 13, 1997, 1046, and Wei, T., Wallace-Freedman, W. G. 5 Schultz, R. G., Xiang, X.-D., Appl. Phys. Lett. 68, 1996, 3506). The disclosure described the preparation of compounds by the deposition process for obtaining various combinations from a substrate by using the masking technique.

The main disadvantage of the method described by Schultz et al. is that when the deposition process is used, only a small part of the possible chemical combinations can be realized, which could be prepared by using conventional catalytic wet chemical processes. This results in the range of possible catalytically active candidates being substantially narrowed. No process has been disclosed for testing catalytically active materials.

In the field of the simultaneous testing of catalysts, there is a publication by Luss et. al. (Moates, F.C., Somani, M., Annamalai, J., Richardson, I. T., Luss, D., Willson, R. C., Ind. Eng. Chem. Res. 35, 1996, 4801) in which catalyst pellets are tested by infrared thermography. However, this method can be used only for reactions with high reaction heat. The selectivity study is not possible.

The invention is based on the problem of providing an apparatus which could be used for efficiently testing the catalytic activity of solids exposed to a reaction gas without high demand for time and labor.

This problem is solved according to the invention by using the characterizing features of claim 1.

An apparatus according to the invention uses simultaneous and consecutive testing of a large number of solid catalysts which are exposed to a reaction gas, wherein the conditions, such as pressure, temperature, etc., can be varied at random.

The apparatus has a receiving device that has a plurality of recesses for receiving individual solids which have to be tested for the catalytic activity. All solids that are in the receiving device are exposed simultaneously to a reaction gas through a common gas supply. The gas flow is discharged through individual gas passages for each recess in such a manner that products that are released over each individual catalyst can be analyzed separately in an analysis device. The analysis can be conducted by using known per se analytical methods such as spectroscopy, spectrometry, or chromatography. During the test phase only one passage can be opened to the analysis device, whereas the gases that are discharged through the remaining passages are not analyzed. The receiving device also allows for analysis of gas flows that are discharged through a plurality of passages. It is also possible to shut off any desired number of passages so that no reaction gases will flow through these passages.

In a preferred embodiment of the receiving device, the recesses are made as a matrix. The arrangement in the form of a matrix not only allows testing a large number of catalysts in a small space,

but it also allows the materials that are being tested to be placed into the recesses by means of a loading device in which catalysts are synthesized and from which they can be then transferred to the receiving devices. It is even possible to synthesize catalysts directly in the receiving *[sic!]* device.

It is preferred that the passages for discharging the gas flows be provided in the bottoms of the recesses in order to assure the passage of the reaction gas through the catalysts.

The loading device for the simultaneous loading of the materials into the recesses has passages per each individual recess, in which catalysts can be prepared in spatially separated manner as per the combinatorial method. In order to assure the closing of the passages of the loading device for conducting the synthesis of solids, it is preferred that a slide gate be provided which can close or open all the passages.

The passages of the loading device are arranged identically to the recesses of the receiving device. For transfer of the solids, the loading device is aligned with the receiving device so that the passages of the loading device are aligned with the recessed of the receiving device.

For pressing the solids from the recesses, the apparatus according to the invention advantageously has a press tool which has press plungers corresponding to the passages of the loading device.

For alignment, the receiving device has a peripheral collar in which the loading device can be inserted. When the loading device is removed, the peripheral collar of the receiving device is provided with a cover to define a common gas supply chamber for the recesses of the receiving device. A reaction gas can be admitted to the common gas supply chamber through a hole in the cover.

In another preferred embodiment, the receiving device has a heating unit to maintain a desired reaction temperature.

Solid catalysts that are to be tested are preferably placed on platelets of a porous material which are installed in the recesses of the receiving device transversally with respect to the flow direction of the reaction gas.

Practical embodiments of the apparatus for testing the catalytic activity of solids exposed to a reaction gas according to the invention will now be described with reference to the accompanying drawings, in which:

Fig. 1 shows a receiving device of an apparatus for testing the catalytic activity of solids exposed to a reaction gas, a sectional view;

Fig. 2 is a sectional view of the receiving device taken along line II-II in **Fig.** 1;

Fig. 3 is a top view of the receiving device shown in **Fig.** 1,

Fig. 4 shows a gas flow diagram for the test apparatus;

Fig. 5 shows a loading device for a test apparatus, a sectional view;

Fig. 6 is a sectional view of the loading device taken along line VI-VI in **Fig.** 5;

Fig. 7 is a slide gate for the loading device of **Fig.** 5, a top view;

Fig. 8 shows a press tool for the test apparatus, a sectional view; and

Fig. 9 shows a comminution device for the test apparatus in a sectional view.

An apparatus for testing the catalytic activity of solids has a receiving device 1 (**Figs.** 1 through 3) in which solid catalysts are exposed to a reaction gas, an analysis device 2, having a valve system 3 (**Fig.** 4), which is used to analyze the products of reactions, and a loading device 4, having a press tool 5, in which the catalysts can be produced in spatially separate locations by using a combinatorial method (**Figs.** 5 through 8).

Fig. 1 shows a sectional view of the receiving device 1 of the test apparatus. The receiving device 1 has a cylindrical body 6 made of a heat conducting material, e.g., preferably brass which has in its upper side cylindrical bores 7 defining an *n x m* matrix with four lines and four columns (**Fig.** 2). The 4x4 matrix is given only as an example, and arrangements with a greater number of recesses can also be used.

Passages 8 are made in the bottom of each recess 7 and lead to the underside of the brass body 6 of the receiving device 1. The passages 8 extend in parallel to each other in the vertical direction. They have a smaller diameter than the recesses. This assures identical flows through all recesses because the passages have appropriate flow resistance. Individual passages can be specially restricted so as to assure exactly the same flow rates through all the recesses. The receiving device can also have special orifices or like devices for the same purpose.

The upper side of the brass body 6 has a flange 9 which is used for holding a cover 10 made of a heat conducting material such as brass. The flange 9 and the cover 10 have a plurality of circumferentially spaced holes 11 which are used for assembling the flange 9 and the cover 10 together by means of bolts (**Fig.** 3). For sealing the cover 10 with the flange 9, a sealing ring 12 is provided in an annular groove 13 of the flange 9.

The brass body 6 and the cover 10 have holes 14 for receiving heating cartridges 15 of a heating unit for heating the receiving device 1 in order to maintain a reaction temperature.

The catalysts that are being tested are each placed on platelets 16 made of a porous inert composition (frit), which are positioned on the bottom of the recesses transversally with respect to their longitudinal axes.

For the simultaneous testing of catalysts, the cover 10 is bolted to the flange 9 of the brass body 6, and a reaction gas is fed through holes 17, 18 of the cover into a gas supply chamber 19 provided over the recesses 7. The reaction gas flows through catalysts 20 which are placed on the frit platelets 16.

Fig. 4 shows a gas flow diagram for the test apparatus. The reaction gas flows from a gas vessel 21 through a gas supply line 22 in which a metering device 23 is inserted and goes to the recesses 7 of the receiving device 1 which is heated by means of a temperature control device 24 to the reaction

temperature in such a manner that the reaction gas flows through the catalysts. The products resulting from the reaction are discharged from each individual catalyst through separate channels 8 separately so as to selectively supply the discharge flows to the analysis device 2.

Multiple-way valves 24 are provided at the outlet of each passage 8. The multiple-way valves are electromagnet actuated and are controlled by means of a controller 25 through control lines 26. The first outlet of each mutiple-way valve 24 is connected through a gas line 27 to a first common gas supply line 28 which leads to the analysis system 2, and the second outlet of each multiple-way valve 24 is connected through a second gas supply line 29 to a second common gas supply line 30 which goes also to the analysis device, e.g., to a mass-spectrometer.

Depending on the switched position of the multiple-way valves, the products resulting from the reaction from each catalyst can be fed separately from each other to the analysis device 2, or the analysis device can analyze the discharge flow from any two catalysts. The valve system which consists of the multiple-way valves can be expanded to any number of valves depending on the quantity of the catalysts that are being tested.

Instead of the valve system used for selectively switching the individual passages, a manipulator with an inlet capillary, which is movable along *xyz*-axes, can be provided downstream of the receiving device 1 and connected to the analysis device. The inlet capillary can be inserted by the manipulator into the passage in such a manner as to analyze each catalyst separately. As a matter of fact, each passage can be connected to a separate analysis device to achieve a high degree of parallelism of the analysis.

Fig. 5 shows a sectional view of the loading device 4 for the test apparatus. The loading device 4 has a two-part cylindrical metal body 31 which has the diameter corresponding to the inside diameter of the flange 9 of the receiving device 1, whereby the loading device 4 can be inserted into the receiving device 1. The cylindrical metal body 31 has a form of a 4x4 matrix of passages 32. The arrangement and the diameter of the passages 32 correspond to the recesses 7 of the receiving device 1 so that they are aligned when the loading device is inserted into the receiving device.

A slide gate 33 is positioned between the upper and lower parts 31a and 31b of the cylindrical metal body for movement transversally with respect to the longitudinal axes of the passages 32. The slide gate 33 is made as a sheet plate with holes 34 which are likewise arranged in the form of a 4 x 4 matrix. These holes 34 are aligned with the passages 32 of the cylindrical metal body 31. Both fasteners 35 which hold the upper and lower parts together extend through lateral longitudinal holes 36 of the slide gate 33 and limit its stroke. The slide gate 33 can move between two positions in which the passages 32 of the loading device are closed or open, respectively.

The slide gate 33 is preferably made of metal. It is also possible to make the slide gate as a perforated plate of a porous material (frit) which is used for filtering when the slide gate is in the position

in which the holes of the perforated plate are not aligned with the passages of the loading device.

Fig. 6 shows a sectional view of the press tool 5 for the test apparatus. The press tool is made as a 4x4 matrix of press plungers 37 which are secured by means of screws 38 to a round plate 39. The press plungers 37 is positioned and sized in such a manner that when the slide gate 33 is open, they can move into the channel 32 of the loading device 4.

Fig. 7 shows a sectional view of a comminution device 40 in the form of a screen that has straight teeth 41 spaced at about 2 mm from each other. The comminution device 40 can be placed in the gas supply chamber 19 of the receiving device 1 before the loading device 4 is inserted into the receiving device so as to comminute the solid material prepared in the loading device when it passes into the receiving device. The comminution device can also be made integral with the loading device.

Oxidation of carbon monoxide with the catalysts prepared by using the combinatorial method using the above-described test apparatus will be described below.

For this test reaction, catalysts prepared by the combinatorial method were tested with carriers such as zeolith Y, aluminum oxide, titanium dioxide, and zirconium oxide in combination with potentially catalytically active metals – platinum and palladium and cerium promoter for a test reaction of catalytic oxidation of carbon monoxide to carbon dioxide. The catalysts were exposed to a reaction gas mixture consisting of synthetic air and 80% carbon monoxide. The reaction atmosphere temperature was raised stepwise, and the product gas flow from each individual passage was analyzed by spectrography for each reaction gas temperature.

The catalysts were synthesized in the top part of the cylindrical body of the loading device with the closed slide gate. In order to do this, a carrier material was placed in each of the four columns, e.g., a silicate carrier was placed in column 1, an aluminum oxide carrier was placed in column 2, a titanium dioxide carrier was placed in column 3, and zirconium oxide carrier was placed in column 4. The catalytically active substances were deposited, e.g., by the impregnation process, e.g., in line 1 a predetermined volume of a platinum salt solution, in line 2 a predetermined volume of a palladium salt solution, in line 3 a predetermined volume of a platinum salt solution and a palladium salt solution, and in line 4 a predetermined volume of a platinum salt solution, and a palladium salt solution, and a cerium salt solution were added. By conducting an appropriate high-temperature treatment, the solvent was removed. A post-processing was then conducted, e.g., with hydrogen. In order to transfer the test array into the receiving device, the comminution device was installed in the gas supply chamber of the loading *[sic!]* device, and the loading device was inserted into the receiving device. When the slide gate was opened, the solid catalysts were pressed by means of the press tool out the passages of the loading device through the screen plate into the recesses of the receiving device. If comminution of the solid materials prepared in the loading device is not required, the step of installation of the comminution device into the receiving

device can be dispensed with. The comminution device and the loading device were then removed from the receiving device. The receiving device was then sealingly closed with the cover, and the reaction gas was supplied. Subsequently, the product gas flow discharged from the catalysts through each individual passage of the receiving device was analyzed by spectroscopy in the analysis device while raising stepwise the temperature of reaction atmosphere.

Claims

1. An apparatus for testing the catalytic activity of a solid exposed to a reaction gas, having a device for receiving solids and a device for analyzing the products formed as a result of the reaction, **characterized by the fact,** that a receiving device (1) comprises a plurality of recesses (7) for receiving each individual solid, a common gas supply, and a passage (8) for each individual recess, whereby all solids are simultaneously exposed to the reaction gas, and the products formed as a result of the reaction can be discharged separately through the passages and can be supplied to an analysis device (2).

2. The apparatus of claim 1, characterized by the fact that the recesses (7) for receiving solids are arranged as a matrix, and the passages (8) are provided in the bottom of the recesses (7) so that the reaction gas can flow through the solids which are placed in the recesses.

3. The apparatus of claim 1 or 2, characterized by the fact that the recesses (7) are cylindrical holes.

4. The apparatus of claims 1 through 3, characterized by the fact that the apparatus has a loading device (4) that can be inserted into the receiving device (1) for simultaneously placing solids into the recesses.

5. The apparatus of claim 4, characterized by the fact that the loading device (4) has passages (32) corresponding as the recesses (7) of the receiving device, in which solids are synthesized and from which the solids can be transferred from the loading device which is inserted into the receiving device to the recesses of the receiving device.

6. The apparatus of claim 5, characterized by the fact that the loading device (4) comprises a slide screen (33) which is movable between the position for synthesizing solids and the position in which the passages are open for transfer of the solids into the recesses (7) of the receiving device.

7. The apparatus of claim 6, characterized by the fact that the slide gate (33) is made as a perforated plate of a metal or a porous material.

8. The apparatus of claims 1 through 7, characterized by the fact that the receiving device (1) has

a peripheral collar (9) in which the loading device (4) can be inserted and a cover (10) which can be mounted on the peripheral collar (9) after removal of the loading device to define a common gas supply chamber (19), the cover having a hole (17) for the admission of a reaction gas .

9. The apparatus of claims 4 through 8, characterized by the fact that the apparatus has a press tool (5) which has press plungers (37) corresponding to the passages (32) of the loading device, which can be inserted into the passages (32) of the loading device for pressing out the solids.

10. The apparatus of claims 1 through 9, characterized by the fact that the receiving device has a heating unit (24).

11. The apparatus of claims 1 through 10, characterized by the fact that the platelets (20) made of a porous material are provided in the recesses (7) of the receiving device (1) for receiving the solids that are transferred.

12. The apparatus of claims 4 through 11, characterized by the fact that the apparatus comprises a comminution device (40) for comminution of the solids which are prepared in the loading device (4) during their transfer into the receiving device (1).

3 sheets of drawings attached

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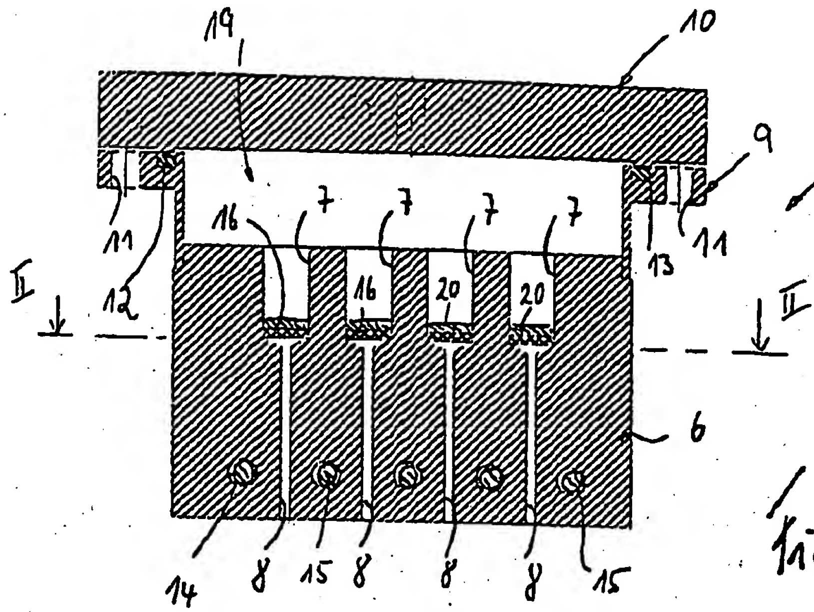

Fig. 1

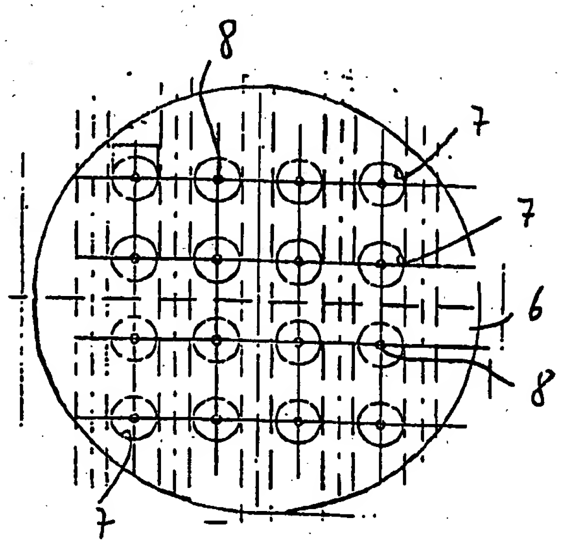

Fig. 2

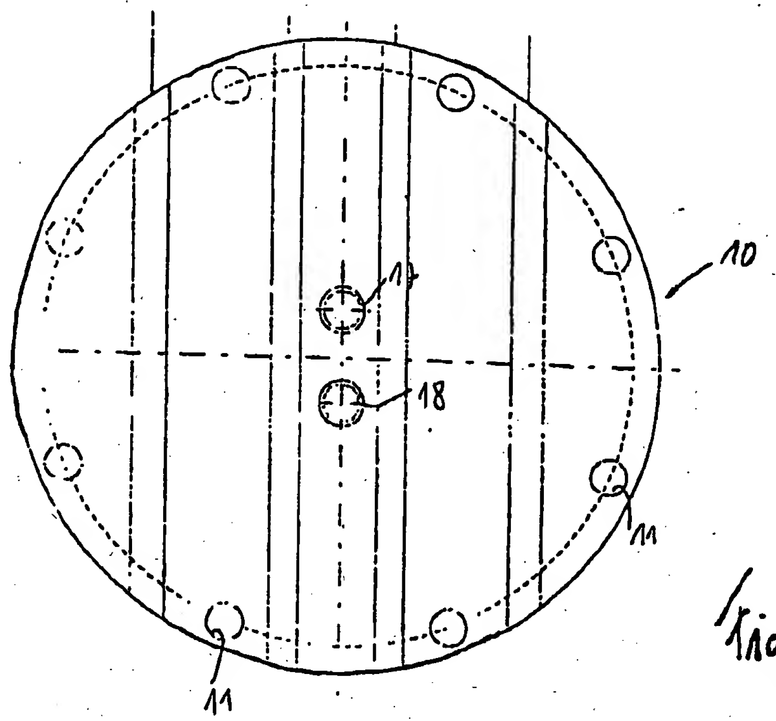

Fig. 3

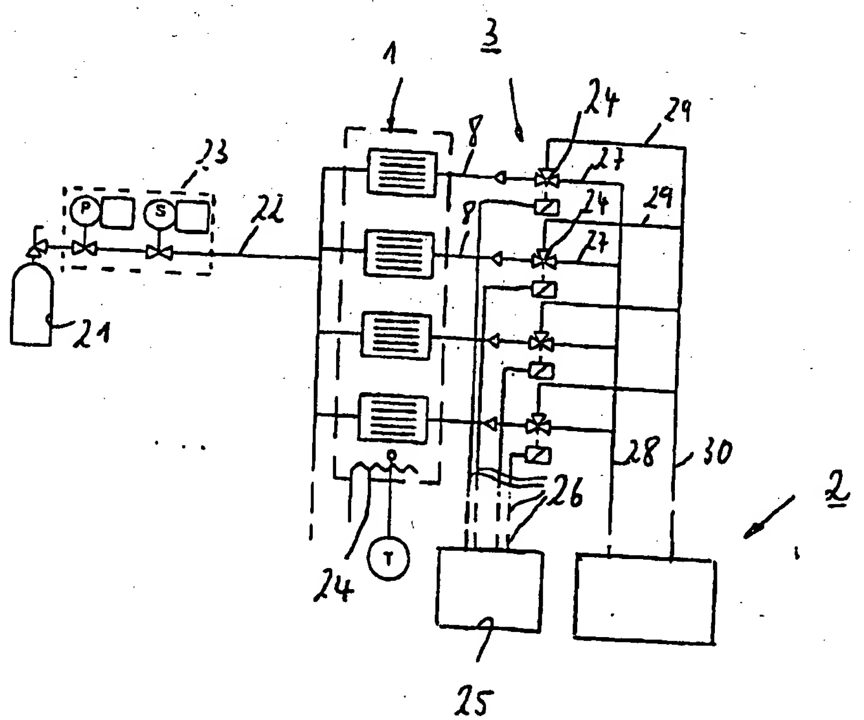

Fig. 4

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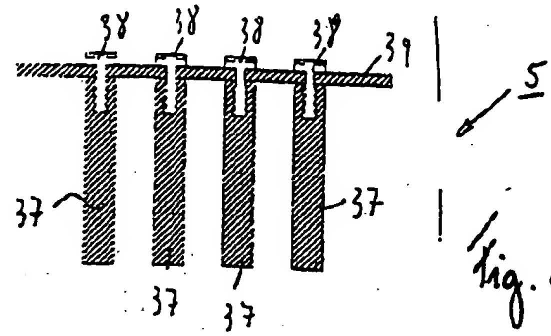

Fig. 8

Fig. 9

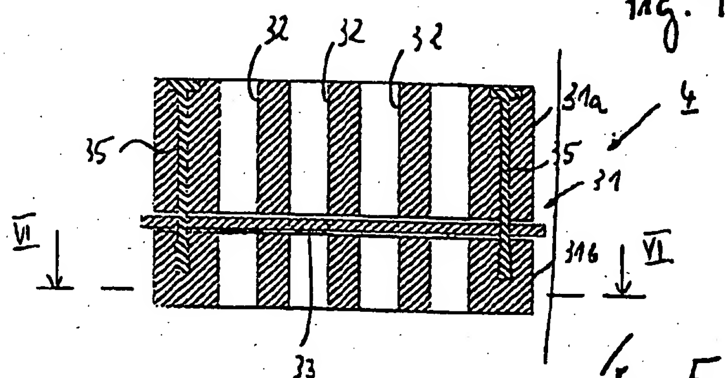

Fig. 5

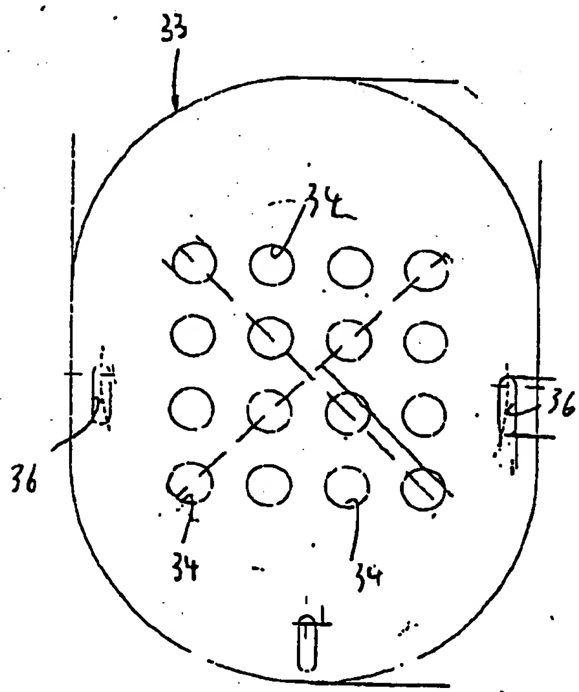

Fig. 7

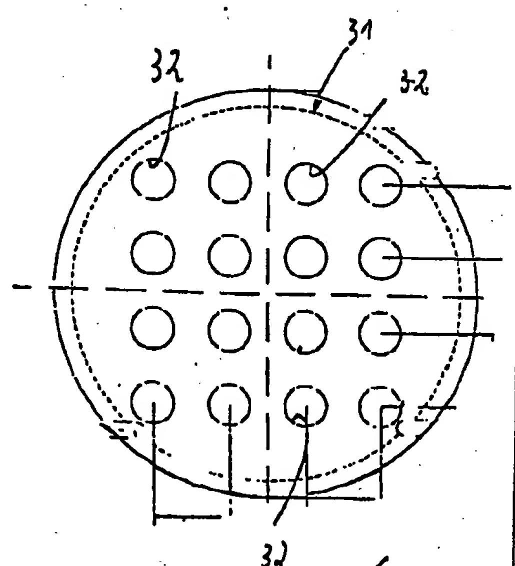

Fig. 6